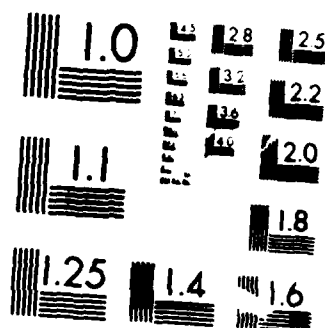AD-A186 974 INTERFACIAL EFFECTS IN THIN LI/PEO CELLS AT ROOM 1/1
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TECHNICAL REPORT No. 2

Interfacial Effects in Thin Li/PEO Cells at Room Temperature

by

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Discharge characteristics and impedance measurements have been obtained for thin film cells comprising lithium and $V_2O_5$ electrodes and a $(PEO)_8 LiClO_4$ electrolyte, and for diagnostic cells with nickel counter electrodes. Results indicate that a reaction layer exists at the Li electrode and that this represents the main limitation to rate capability of the cells at room temperature.

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# Interfacial Effects in Thin Li/PEO Cells at Room Temperature

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## Introduction

We have previously reported the fabrication and preliminary discharge characteristics of thin film storage devices based on the following structure[1]:

$$Ni \mid Li \mid (PEO)_8 LiClO_4 \mid V_2O_5 \mid Ni$$
$$1\mu m \quad 1\mu m \quad\quad 4\mu m \quad\quad .1-.2\mu m \quad 1\mu m$$
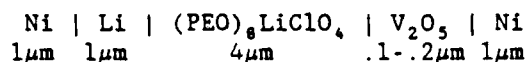
In the present studies the discharge characteristics of such devices have been investigated further to identify the features which determine cell performance. These have been complemented by impedance measurements, not only on the storage device itself but also on a diagnostic cell with the same structure as the above cell less the $V_2O_5$ insertion electrode, in order to quantify resistances at the lithium/polymer interface.

## Experimental

Both storage devices and diagnostic cells have been fabricated using established thin film deposition techniques. The substrates were either 3" silicon wafers insulated by a 1-2$\mu m$ layer of thermally grown $SiO_2$, or glass slides. Nickel electrical contact tracks were evaporated thermally through a mask to a thickness of approximately 1$\mu m$, as shown in Figure 1a. For the storage device only, $V_2O_5$ was deposited through another mask onto the positive contact by evaporation; in this process some oxygen was invariably lost to the pumping system giving a slightly reduced layer, $V_2O_{5-x}$; the structure after this step is shown in Figure 1b. In both the storage and diagnostic devices a 4% solution of $(PEO)_3LiClO_4$ was applied across the contacts by dip coating in an argon atmosphere, using PTFE tape as a mask; after the solvent has been evaporated a thin polymeric film is left, approximately 4$\mu m$ thick (as determined by SEM), as shown in Figure 1c. Using a standard thermal evaporator, housed in a sealed box under an argon atmosphere, the lithium bridging contact was made (Figure 1d). The cells were produced in arrays to facilitate connection to a data logging and the complex impedance systems, and the layout is shown in Figure 1e. Each cell had an effective surface area of 12mm$^2$.

## Results and Discussion

The reliability of the storage cells has improved considerably since the earlier report[1]. Using a 4$\mu m$ polymer layer to prevent a short circuit, and Ni current collectors to avoid the previous problem of the reaction of Pt with Li, the yield of working cells now approaches 100%. Discharge curves for the storage cells for various currents are shown in Figure 2. Each curve has an almost immediate 'IR drop' followed by a steady decrease in voltage dependent on the total charge passed. The 'IR drop' is not exactly proportional to current, as an additional over-potential of around 0.2V appears as well as the ohmic contribution corresponding to about 10k$\Omega$.

The discharge curves can be rationalised by subtracting the effect due solely to the 'IR drop', and thereafter plotting voltage as a function of the charge that has been passed, as in Figure 3. Here it may be seen that at $1\mu A$ a maximum capacity corresponding to insertion of about 4 Li per $V_2O_5$ is obtained as the voltage decreases to 1.5V. This may be taken as the EMF to composition relation for the insertion reaction. The EMF values are rather higher than expected, and it is conceivable that the additional overpotential described above may be due to the very steep initial portion of the EMF curve.

At greater discharge currents the curves start to follow the EMF curve, but deviate downwards after the passage of a critical amount of charge. A normal diffusion overpotential in the positive electrode should not show this behaviour, but an increase in the initial slope proportional to the current. It will be shown that the results can be explained by a limiting current effect in the electrolyte. A previous analysis[2] by one of the authors has pointed out that a limiting current phenomenon should be seen in a solid electrolyte if the current exceeds that corresponding to an ohmic drop of about 0.1t+ volts, where t+ is the transport number of the inserted ion. With t+ = 0.3 and R = $10k\Omega$, we expect the limiting current to be approximately $3\mu A$. This is consistent with the absence of deviation from the EMF curve when the discharge current was below this figure.

Complex impedance results on the diagnostic cells are shown in Figure 4. The two depressed semi-circles are due firstly to the polymer electrolyte and secondly to a reaction product between Li and the polymer. From an analysis of the frequency dependence of the impedance it may be deduced that the first small semi-circle is caused by the polymer, and the second larger one by the reaction product, as reported by Fauteux & Gauthier[3]. The resistance due to the product also increased with time with roughly a $\sqrt{t}$ dependance, as shown in Figure 5. Impedance results from the storage cells were in general similar to those of the diagnostic cells, indicating that the resistive effects are mainly due to a reaction layer at the Li electrode rather than the polymer itself. This means that the limiting current effect is derived from this same layer, and therefore it is this layer which restricts the rate capability of these and other PEO cells at room temperature.

Other polyethers are now being investigated in order to improve the cell performance. Early experiments with poly(propylene oxide), marketed as Parel 58 by Hercules Inc., have given much larger interfacial impedances, as shown in Figure 6. An amorphous ethylene oxide co-polymer with a high conductivity reacted even more quickly with the evaporated Li, such that the Li film was completely degraded shortly after deposition.

## Conclusion

Thin film cells can be constructed with good reliability, and the performance limiting factor has been identified as the interfacial reaction layer. The long term storage life of these, and other Li/polymer cells, will, however, be dependent on suppression of the interfacial corrosion reaction.

## Acknowledgments

## References

1) J R Upton et al, Extended Abstracts, ECS Fall Meeting, San Diego (1986)

2) J R Owen et al, Extended Abstracts, ECS Spring Meeting, San Francisco (1986)

3) D Fauteux & M Gauthier, Extended Abstracts, ECS Fall Mtg, San Diego (1986)
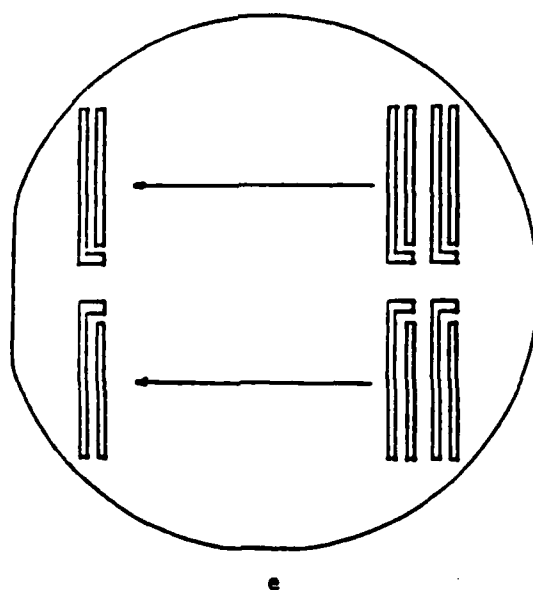
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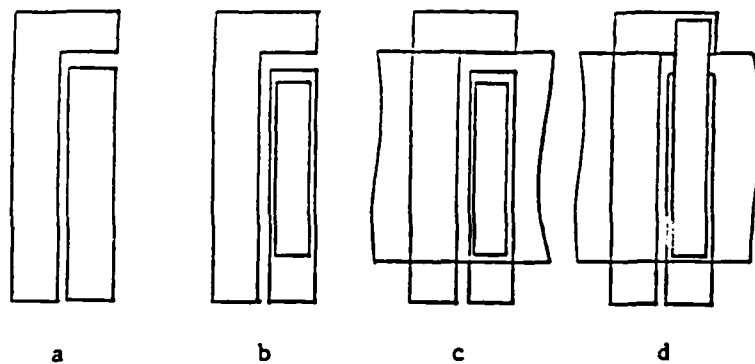e

Figure (1).  Cell Fabrication Method.
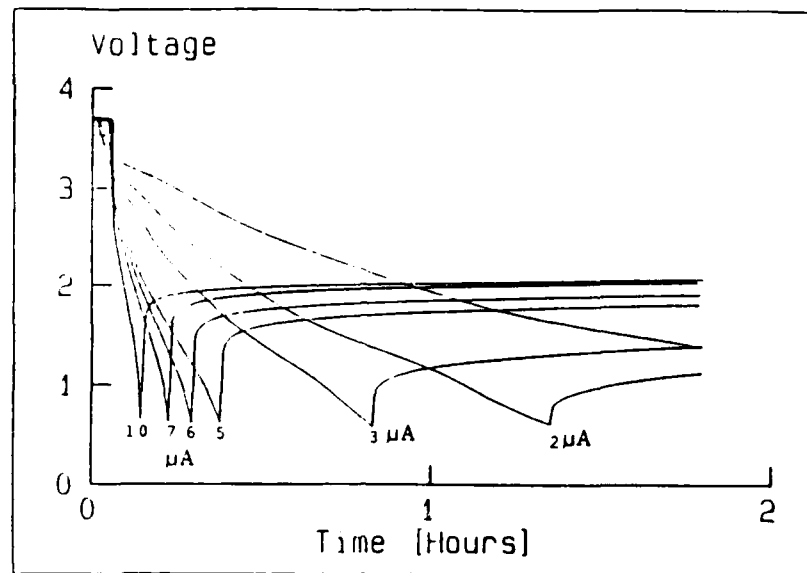
Figure (2).     Constant Current Discharge of Storage
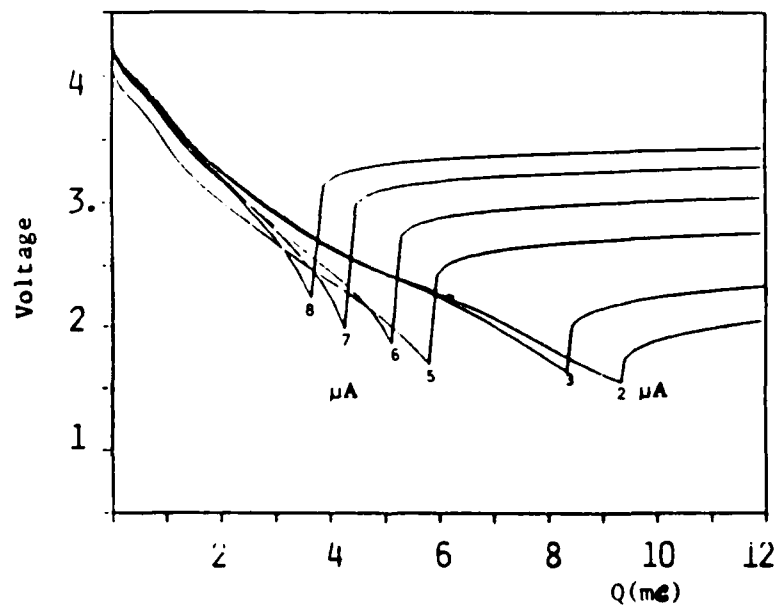                Devices.



Figure (3).     V+IR vs Q for Storage Devices

Figure (4)
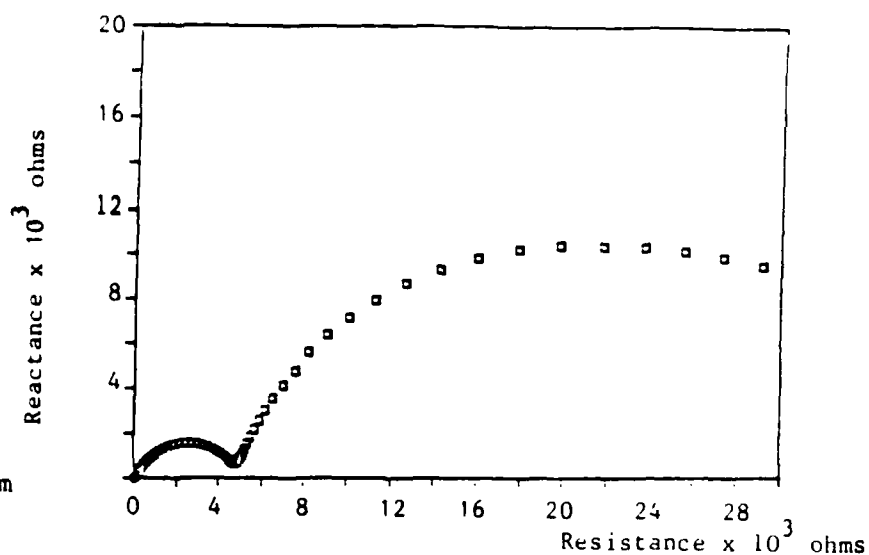Impedance Spectrum
of
Diagnostic cell



Figure (5)
Resistance of the
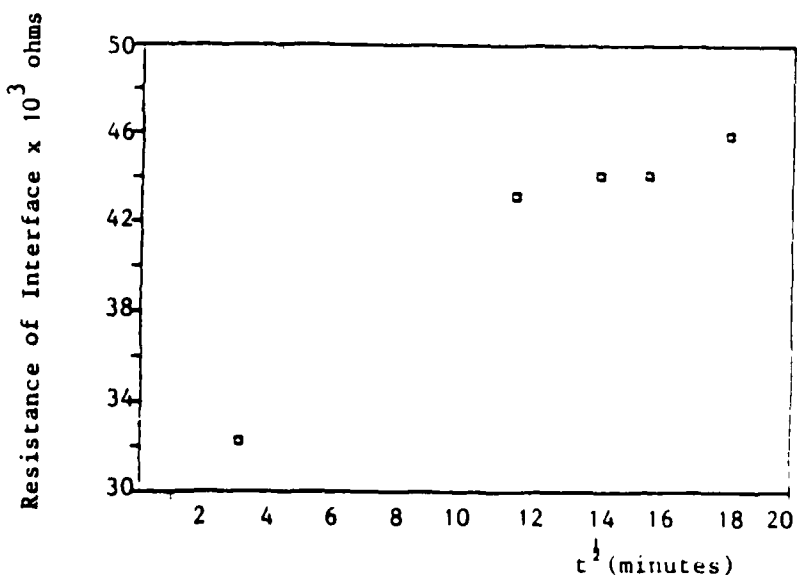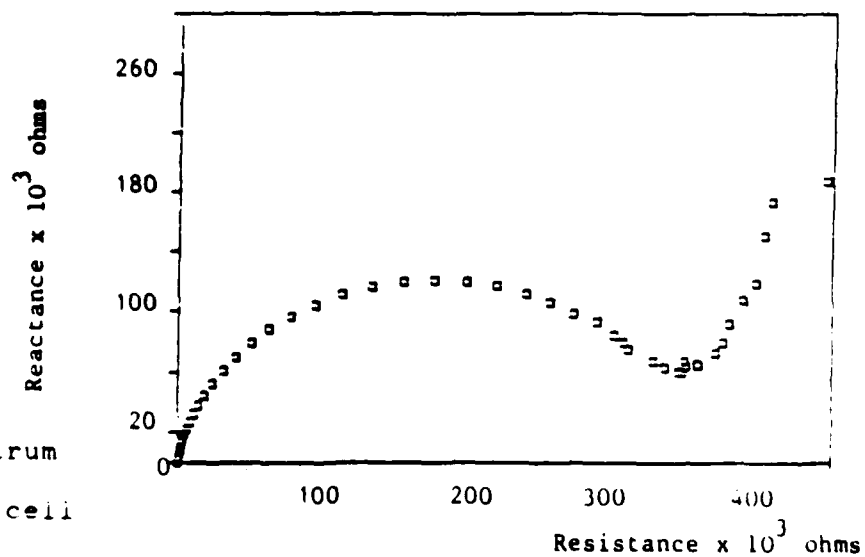Interface as a
Function of $t^{1/2}$



Figure (6)
Impedance Spectrum
of
PPO Diagnostic cell

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